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CLAIMS

[Claim(s)]

[Claim 1] The alkali fusibility novolak resin with which a part of hydrogen atom of all phenolic hydroxyl groups is permuted by 1 and 2-naphthoquinonediazide sulfonyl group, and the positive type photoresist constituent which comes to contain an acid generator.

[Claim 2] Said alkali fusibility novolak resin is a positive type photoresist constituent according to claim 1 characterized by for the polystyrene equivalent weight average molecular weight (Mw) by gel-permeation-chromatography (GPC) measurement being 4000-5000, and degree of dispersion [weight-average-molecular-weight (Mw) / number average molecular weight (Mn)] being 3.0 or less.

[Claim 3] Said alkali fusibility novolak resin is a positive type photoresist constituent according to claim 1 or 2 with which 3.0-5.0-mol% of the hydrogen atom of all phenolic hydroxyl groups is characterized by permuting by 1 and 2-naphthoquinonediazide sulfonyl group.

[Claim 4] Said alkali fusibility novolak resin is a positive type photoresist constituent given in claim 1 characterized by being the esterification object of the phenol novolak resin whose content of a dimer the content of a phenol system monomer is 1 or less % of the weight, and is 4 or less % of the weight, and 1 and 2-naphthoquinonediazide sulfonic-acid compound thru/or any 1 term of 3.

[Claim 5] The substrate with the photosensitive film with which the photosensitive film of 3.0 micrometers or more of thickness formed in claim 1 thru/or any 1 term of 4 using the positive type photoresist constituent of a publication is characterized by being formed on a substrate.

[Claim 6] The formation approach of the resist pattern characterized by performing alternative exposure which used i line (365nm) for the light source on the photosensitive film of 6.0 micrometers or more of thickness formed on the substrate using the positive type photoresist constituent given in claim 1 thru/or any 1 term of 4, and forming a pattern in it.

[Claim 7] Said pattern is the formation approach of the resist pattern according to claim 6 characterized by being a tooth-space pattern with a width of face of 0.8 micrometers or less.

[Claim 8] (1) The process which forms the coat of the acid cross-linking ingredient which causes crosslinking reaction by operation of an acid all over the formed pattern according to claim 6 or 7, (2) by removing said acid cross-linking ingredient of the process over which the part which touches the pattern of said acid cross-linking ingredient according to an operation of the acid which is heat-treated and is diffused from a pattern front face is made to construct a bridge, and the field which is not constructing a bridge with (3) developers The formation approach of the resist pattern characterized by having the process which forms the pattern of width of face narrower than the tooth-space width of face of the pattern before forming the coat of an acid cross-linking ingredient.

[Claim 9] (1) The process which forms the coat of the acid cross-linking ingredient which causes crosslinking reaction by operation of an acid all over the formed pattern according to claim 6 or 7, (2) The process which the complete exposure or alternative exposure by UV irradiation is performed [process], and makes a pattern front face or the interior generate an acid, (3) by removing said acid cross-linking ingredient of the process over which the part which touches the pattern of said acid cross-linking ingredient according to an operation of the acid which is heat-treated and is diffused from a pattern front face is made to construct a bridge, and the field which is not constructing a bridge with (4) developers The formation approach of the resist pattern characterized by having the process which forms the pattern of width of face narrower than the tooth-space width of face of the pattern before forming the coat of an acid cross-

linking ingredient.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] About the formation approach of a positive type photoresist constituent, a substrate with the photosensitive film, and a resist pattern, this inventions are especially thick-film conditions, and relate to the formation approach of the suitable positive type photoresist constituent for the production process of the magnetic head for magnetic disk drives, such as a huge magnetic-reluctance (GMR:Giant Magnetoresistive) head which needs formation of the pattern which is excellent in perpendicularity, and a magnetic-reluctance (MR:Magnetoresistive) head, a substrate with the photosensitive film, and a resist pattern.

[0002]

[Description of the Prior Art] The photoresist constituent which consists of alkali fusibility resin and a quinone diazide radical content compound until now Although manufacture of a semiconductor device or a liquid crystal device is enough presented in a photolithography techniques using i line (365nm) at practical use since it excels in definition, sensibility, and etching-proof nature In the field which forms the up magnetic pole of the magnetic heads, such as the manufacture field which needs a thick-film process, for example, a GMR head, and an MR head, especially a recording head (magnetic head) Under about 6.0-8.0-micrometer thick-film conditions, especially 3.0 micrometers or more the tooth-space pattern with a width of face of 0.8 micrometers or less of a high aspect ratio To form with sufficient perpendicularity is needed and it is made difficult using the positive type photoresist constituent for the conventional i lines to form the tooth-space pattern of a high aspect ratio with sufficient perpendicularity under such thick-film conditions.

[0003] Moreover, JP,2-63059,A, JP,5-166717,A, JP,5-241348,A, JP,6-250379,A, JP,7-124422,A, JP,7-281449,A, JP,9-270377,A, JP,10-73927,A, To JP,10-163093,A, JP,11-204399,A, JP,11-283905,A, and JP,11-283910,A According to an operation of the acid which forms and heat-treats the 2nd resist coat on the tooth-space pattern front face of a low aspect ratio, and is diffused from the above-mentioned interior of a tooth-space pattern By making the resist coat of the above 2nd insolubilize (bridge formation), the technique in which width of face can form a tooth-space pattern 0.5 micrometers or less is indicated on the thin film conditions of about 0.5-1.5 micrometers of thickness.

[0004] However, under about 6.0-8.0-micrometer thick-film conditions, formation of the tooth-space pattern which is excellent in thermal resistance was especially difficult, and 3.0 micrometers or more of things for which film contraction takes place and the good tooth-space pattern of perpendicularity is formed during heat-treatment were difficult. Moreover, especially, the generating effectiveness of an acid was bad and there were 3.0 micrometers or more of problems which do not advance so that bridge formation may consider under about 6.0-8.0-micrometer thick-film conditions. Furthermore, in order to raise the generating effectiveness of an acid, when the above-mentioned heat-treatment was performed at the elevated temperature, there was a problem which gives thermal degradation to other component parts which constitute the magnetic head.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, especially the purpose of this invention is to offer the formation approach of the positive type photoresist constituent in which it excels in thermal resistance, and formation of a tooth-space pattern with the sufficient generating effectiveness of an acid is possible under about 6.0-8.0-micrometer thick-film conditions, and 3.0 micrometers or more of things for which the tooth-space pattern which is a high aspect ratio with a width of face of 0.8 micrometers or less is formed with sufficient perpendicularity are possible, a substrate with

the photosensitive film, and a resist pattern.

[0006]

[Means for Solving the Problem] this invention persons acquired solving the aforementioned technical problem, as a result of inquiring wholeheartedly.

[0007] That is, this invention offers the alkali fusibility novolak resin with which a part of hydrogen atom of all phenolic hydroxyl groups is permuted by 1 and 2-naphthoquinonediazide sulfonyl group, and the positive type photoresist constituent which comes to contain an acid generator.

[0008] Moreover, the polystyrene equivalent weight average molecular weight (M_w) according [said alkali fusibility novolak resin] to gel-permeation-chromatography (GPC) measurement in this invention is 4000-5000, and offers the aforementioned positive type photoresist constituent characterized by degree of dispersion [weight-average-molecular-weight (M_w) / number average molecular weight (M_n)] being 3.0 or less.

[0009] Moreover, as for this invention, said alkali fusibility novolak resin offers the aforementioned positive type photoresist constituent characterized by permuting 3.0-5.0-mol% of the hydrogen atom of all phenolic hydroxyl groups by 1 and 2-naphthoquinonediazide sulfonyl group.

[0010] Moreover, the content of a phenol system monomer of said alkali fusibility novolak resin is 1 or less % of the weight, and, as for this invention, the content of a dimer offers the aforementioned positive type photoresist constituent characterized by being the esterification object of the phenol novolak resin which is 4 or less % of the weight, and 1 and 2-naphthoquinonediazide sulfonic-acid compound.

[0011] Moreover, this invention offers the substrate with the photosensitive film with which the photosensitive film of 3.0 micrometers or more of thickness formed using the aforementioned positive type photoresist constituent is characterized by being formed on a substrate.

[0012] Moreover, this invention performs alternative exposure which used i line (365nm) for the light source on the photosensitive film of 6.0 micrometers or more of thickness formed on the substrate using the aforementioned positive type photoresist constituent, and offers the formation approach of the resist pattern characterized by forming a tooth-space pattern.

[0013] Moreover, this invention offers the formation approach of the aforementioned resist pattern characterized by said pattern being a tooth-space pattern with a width of face of 0.8 micrometers or less.

[0014] Moreover, the process in which this invention forms the coat of the acid cross-linking ingredient which causes crosslinking reaction by operation of an acid all over the pattern with which (1) above was formed, (2) by removing said acid cross-linking ingredient of the process over which the part which touches the pattern of said acid cross-linking ingredient according to an operation of the acid which is heat-treated and is diffused from a pattern front face is made to construct a bridge, and the field which is not constructing a bridge with (3) developers The formation approach of the resist pattern characterized by having the process which forms the pattern of width of face narrower than the tooth-space width of face of the pattern before forming the coat of an acid cross-linking ingredient is offered.

[0015] Moreover, the process in which this invention forms the coat of the acid cross-linking ingredient which causes crosslinking reaction by operation of an acid all over the pattern with which (1) above was formed, (2) The process which the complete exposure or alternative exposure by UV irradiation is performed [process], and makes a pattern front face or the interior generate an acid, (3) by removing said acid cross-linking ingredient of the process over which the part which touches the pattern of said acid cross-linking ingredient according to an operation of the acid which is heat-treated and is diffused from a pattern front face is made to construct a bridge, and the field which is not constructing a bridge with (4) developers The formation approach of the resist pattern characterized by having the process which forms the pattern of width of face narrower than the tooth-space width of face of the pattern before forming the coat of an acid cross-linking ingredient is offered.

[0016]

[Embodiment of the Invention] (A) As for (A) alkali fusibility novolak resin used for alkali fusibility novolak resin this invention, a part of hydrogen atom of all phenolic hydroxyl groups is permuted by 1 and 2-naphthoquinonediazide sulfonyl group. (A) A component may be compounded by the esterification reaction of the polycondensation product compounded by the dehydration condensation reaction of a phenolic compound and a condensing agent, and 1 and 2-naphthoquinonediazide sulfonic-acid compound (refer to JP,10-97066,A).

[0017] In that case, it is desirable to use the phenolic compound in which the alkyl group carried out 1-3-piece nuclear substitution to the phenolic compound used, for example, it can mention o-cresol, m-cresol, p-cresol, 2, 5-xylenol, 3, 4-

xylenol, 3,5-xylenol, 2 and 3, a 5-trimethyl phenol, etc. to it. At least one sort as which especially suitable novolak resin is chosen from m-cresol; p-cresol and 3, and 4-xylenol; It is novolak resin compounded using at least one sort chosen from a 2, 3, and 5-trimethyl phenol and 3,5-xylenol. Especially the novolak resin compounded using the phenolic compound of these plurality is suitable when forming 3.0 micrometers or more of tooth-space patterns with a width of face of 0.8 micrometers or less which is excellent in thermal resistance of a high aspect ratio with sufficient perpendicularity under about 6.0-8.0-micrometer thick-film conditions. (A) alkali fusibility novolak resin compounded even especially in inside using m-cresol, p-cresol and 2 and 3, and a 5-trimethyl phenol excels in sensibility, definition, and the perpendicularity of a tooth-space pattern cross-section configuration and is desirable.

[0018] moreover, at least one sort as which the (A) component is chosen from 25-55 mol %; p-cresol system unit and 3, and 4-xylenol system unit in m-cresol system unit among [all] a phenol system configuration unit -- 15 - 45-mol %; -- it is desirable to contain at least one sort chosen from a 2, 3, and 5-trimethyl phenol system unit and a 3,5-xylenol system unit in [15 - 45 mol] %. When there is an inclination for sensibility and thermal resistance to be inferior in m-cresol system unit being less than [25 mol %] and 55-mol % is exceeded, there is an inclination for film decrease to become large. Moreover, when there is an inclination for definition to fall that at least one sort of configuration units chosen from p-cresol system unit and 3, and 4-xylenol system unit are less than [15 mol %] and 45-mol % is exceeded, sensibility and thermal resistance are inferior, and there is an inclination which Society for Cutting Up Men generates. Moreover, when there is an inclination for the perpendicularity of a tooth-space pattern (resist pattern) cross-section configuration and thermal resistance to be inferior in at least one sort of configuration units chosen from a 2, 3, and 5-trimethyl phenol system unit and a 3,5-xylenol system unit being less than [15 mol %] and 45-mol % is exceeded, there is an inclination for sensibility to fall remarkably.

[0019] As said condensing agent, the aldehydes used for composition of phenol novolak resin from the former and ketones are mentioned, and aldehydes, especially formaldehyde are used suitably especially. After performing the dehydration condensation reaction of a phenolic compound and a condensing agent, by well-known judgment actuation, a low-molecular-weight region is cut, polystyrene equivalent weight average molecular weight (M_w) is 4000-5000, and degree of dispersion [weight-average-molecular-weight (M_w) / number average molecular weight (M_n)] considers as 3.0 or less phenol novolak resin.

[0020] in addition, the thing for which judgment actuation is performed so that the content of a phenol system monomer may be 1 or less % of the weight and the content of a dimer may become 4 or less % of the weight at this time -- things are desirable. It is [an inclination for the perpendicularity of a tooth-space pattern cross-section configuration to be inferior when the content of a phenol system monomer and a dimer exceeds this range, and to generate residue (Society for Cutting Up Men) on the substrate after development, and for thermal resistance to fall] and is not desirable. In addition, the content of a phenol system monomer and a dimer can be checked from the result of gel-permeation-chromatography (GPC) measurement. That is, from a GPC chart, the molecular weight distribution of compound phenol novolak resin can be checked, and each content can be computed by measuring the intensity ratio of the peak applicable to a phenol system monomer and the elution time amount of a dimer. In addition, since a phenol system monomer and the elution time amount of a dimer change with measurement means, specification of a column, an eluate, a flow rate, temperature, a detector, sample concentration, an injection rate, a measuring instrument, etc. is important for them. In addition, in this invention, by using the following measurement means, the elution time amount of a phenol system monomer can belong near for 23 to 25 minutes, and the elution time amount of a dimer can belong near for 21 to 22 minutes, respectively.

[0021] [The measurement means of GPC in this invention]

(1) Dissolve 20mg of samples in THF10ml, and adjust the sample solution.

10micro of sample solutions 1 of (2) and (1) was poured into the following GPC measuring device, and the elution time amount of the sample which passes for 28 minutes and is detected near UV wavelength of $\lambda = 280\text{nm}$ was measured.

(Measuring device) a guard column (product made from product name "KF-G";Shodex), and three separation columns (column size 8micrometer(path) x which used the styrene-divinylbenzene copolymer of 6-micrometer particle size as the bulking agent -- 300mm (die length)) It has a product made from product name "KF-801";Shodex. Separation column temperature The liquid-sending rate of the eluate of a tetrahydrofuran (THF) was performed on condition that 1.0 ml/min using the GPC measuring device (product made from product name "GPC SYSTEM 11";Shodex) set as 40 degrees C using oven.

[0022] Moreover, as 1 which may be used for an esterification reaction with said phenol novolak resin, and a 2-naphthoquinonediazide sulfonic-acid compound, halogenides, such as quinone diazide compounds, such as 1, 2-naphthoquinonediazide-4-sulfonic-acid chloride, 1, and 2-naphthoquinonediazide-5-sulfonic-acid chloride, are mentioned, for example.

[0023] There is also an inclination for the perpendicularity of a cross-section configuration to worsen because definition will fall if, as for an esterification reaction, it is desirable that 3.0-5.0-mol % of the hydrogen atom of all phenolic hydroxyl groups is permuted by 1 and 2-naphthoquinonediazide sulfonyl group, and 5.0-mol % is exceeded preferably less than [3.0 mol %], since the film decrease inclination for breadth and an unexposed part has the large tooth-space pattern upper part, and the tooth-space pattern upper part spreads, and to cause degradation of sensibility, and it is not desirable.

[0024] (A) Although especially a component is not restricted, in order to form a tooth-space pattern with a width of face of 0.8 micrometers or less with sufficient perpendicularity in about 6.0-8.0-micrometer thick-film conditions especially, it is desirable that polystyrene equivalent weight average molecular weight (Mw) is [4000-5000, and degree of dispersion [weight-average-molecular-weight (Mw) / number average molecular weight (Mn)]] 3.0 or less and that Mw is [4100-4500, and Mw/Mn] 2.2-2.8 preferably 3.0 micrometers or more.

[0025] The perpendicularity of a cross-section configuration worsens because the tooth-space pattern upper part spreads that Mw is less than 4000, film decrease of an unexposed part remarkable at the time of development takes place, and there is an inclination for definition and thermal resistance to be inferior. Moreover, when Mw exceeds 5000, the perpendicularity of the cross-section configuration of a tooth-space pattern worsens similarly, definition deteriorates, and it is in the inclination for sensibility to also fall. Moreover, when Mw/Mn exceeds 3.0, breadth and definition deteriorate and the tooth-space pattern upper part is in the inclination for the perpendicularity of a tooth-space pattern cross-section configuration to worsen. Especially this inclination is notably seen, when it shifts to a focus's of light at time of exposure plus side (when a focus shifts to the pars-basilaris-ossis-occipitalis side of a resist coat), and a depth of focus width-of-face property falls as a result.

[0026] (B) Bulk effect of a resist coat, i.e., the bias of a film consistency, can be make small by blend at least one sort choose by request in a high-boiling point organic solvent and this invention from high-boiling point [that the boiling point be about 200-350 degrees C] organic solvents, the tooth-space pattern which be excellent at perpendicularity even when the resist coat of a thick film be form on the substrate which have a level difference in a front face using a positive type photoresist constituent can be form, and it be desirable. Moreover, it attains [formation of a good tooth-space pattern] ** [according to / the conditions (heating time, heating means, etc.) of prebaking processing and exposure afterbaking (PEB) processing] and is desirable.

[0027] As a high-boiling point organic solvent, for example (B) Benzyl acetate, isoamyl salicylate, A methyl salicylate, benzyl salicylate, a diethyl phthalate, dibutyl phthalate, A dimethyl phthalate, gamma-butyrolactone, ethyl benzoate, benzoic-acid butyl, Benzoic-acid propyl, benzyl benzoate, ethylene glycol monophenyl ether, The ethylene glycol mono-hexyl ether, 1, 3-octylene glycol, A diethylene glycol, diethylene-glycol diacetate, diethylene-glycol dibutyl ether, Diethylene glycol monoethyl ether, diethylene glycol monoethyl ether acetate, The diethylene-glycol monobutyl ether, diethylene glycol monobutyl ether acetate, Dipropylene glycol, the dipropylene glycol monobutyl ether, Triethylene glycol, triethylene glycol di-2-ethylbutyrate, Triethylene glycol wood ether, the triethylene glycol monoethyl ether, The triethylene glycol monomethyl ether, tripropylene glycol, tripropylene glycol monomethyl ether, 2-ethylhexanoic acid, a caprylic acid, a caproic acid, a catechol, octyl phenol, N-methyl pyrrolidone, etc. can be mentioned. These may be independent, or two or more sorts may be mixed and they may be used. That whose boiling point is 250-350 degrees C especially is desirable, and especially benzyl salicylate is suitable. (B) The loadings of a high-boiling point organic solvent are deficient in the effectiveness of suppressing the above-mentioned phenomenon to the total quantity of the alkali fusibility novolak resin (above-mentioned [A]) and the following (D) sensitizer blended by request as 6 - 12 % of the weight is especially desirable and it is less than 3 % of the weight three to 15% of the weight, and if they exceed 15 % of the weight, they worsen [the perpendicularity of a cross-section configuration] by the tooth-space pattern upper part spreading etc. and are not desirable.

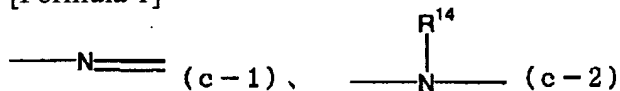
[0028] (C) In adhesion improver this invention, in order to raise adhesion with a substrate, the adhesion improver indicated by JP,62-262043,A, JP,11-223937,A, etc. may be blended. For example, 6-methyl-8-hydroxyquinoline, 6-ethyl-8-hydroxyquinoline, 5-methyl-8-hydroxyquinoline, 8-hydroxyquinoline, 8-acetyloxy quinoline, A 4-hydroxy pteridine, 2, 4-dihydroxy pteridine, and 4-hydroxy pteridine-2-sulfonic acid, A 2-ethyl-4-hydroxy pteridine, a 2-

methyl-4-hydroxy pteridine, 1, 10-phenanthroline, 5, the 6-dimethyl -1, 10-phenanthroline, 3, the 8-dimethyl -1, 10-phenanthroline, 3, 8-dihydroxy -1, 10-phenanthroline, The 5-carboxy -1, 10-phenanthroline, 5, 6-dihydroxy -1, 10-phenanthroline, 1, a 10-phenanthroline-5-sulfonic acid, 4, the 4'-dimethyl -2, a 2'-bipyridyl, a 2 and 2'-bipyridyl, and 2 and 2 -- a - bipyridyl-5-carboxylic acid, and '5, 5' - dichloro -2 and - bipyridyl, and 2 '3, 3'-dihydroxy - 2 and 2 - bipyridyl, and '3, 3' - dimercapto-2 and 2' - bipyridyl etc. is mentioned.

[0029] Moreover, the adhesive property over the substrate of a positive type photoresist constituent can be remarkably raised especially on a ring by blending the heterocyclic compound of the aromaticity which has at least one from association expressed in the following general formula (c-3) as at least one from the following general formula (c-1) and (c-2) association expressed.

[0030]

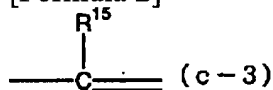
[Formula 1]



[0031] (R14 expresses the alkyl group of a hydrogen atom or the carbon atomic numbers 1-3 among a formula)

[0032]

[Formula 2]

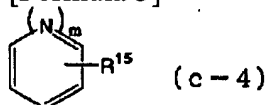


[0033] (R15 expresses among a formula the straight chain of the carbon atomic numbers 1-5 which the hydroxyl group or the hydroxyl group permuted, or a branching-like alkyl group)

[0034] As said heterocyclic compound, it is an "organic compound structure-expression index" (issue on December 20, Showa 52), for example. The Indore system compound indicated by pp.362-401 of Maruzen Co., Ltd., What has 5 membered-ring frame of nitrogen 1 atoms, such as an indoline system compound and an indigo system compound; A pyridine system compound, A quinoline system compound, a hydronalium quinoline system compound, an isoquinoline system compound, An acridine system compound, a benzoquinoline system compound, a naphth quinoline system compound, What has 6 membered-ring frame of nitrogen 1 atoms, such as a phenanthroline system compound; A pyrazole system compound, What has 5 membered-ring frame of nitrogen 2 atoms, such as an imidazole system compound, an imidazoline system compound, and a benzimidazole system compound; A diazine system compound, What has 6 membered-ring frame of nitrogen 2 atoms, such as a hydronalium pyridine system compound, a benzodiazine system compound, and a dibenzo diazine system compound; A triazole compound, What has 6 membered-ring frame of nitrogen 3 atoms, such as thing; triazine compound which has 5 membered-ring frame of nitrogen 3 atoms, such as a benzotriazol system compound; Tetrazole, What has 6 membered-ring frame of nitrogen 4 atoms, such as thing; 1 which has 5 membered-ring frame of nitrogen 4 atoms, such as pentetrazol, 2 and 4, and 5-tetrazine; in addition to this, a pudding system compound, a pteridine system compound, an alloxazine system compound, a 2H-pyrrole, etc. are mentioned. Also in these, the compound expressed with the following general formula (c-4) is desirable at the point that the positive type photoresist constituent which controlled generating of Society for Cutting Up Men, and was excellent in the adhesive property over a substrate can be offered, and especially 2-(2-hydroxyethyl) pyridine is desirable.

[0035]

[Formula 3]



[0036] (Among a formula, m expresses the integer of 1-3 and R15 expresses the same semantics as the above)

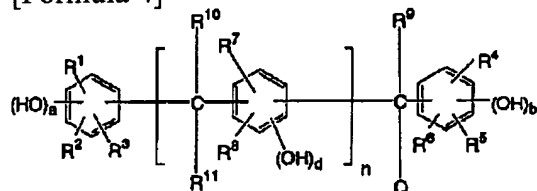
[0037] (C) As opposed to the total quantity of the following (D) sensitizer with which the addition of an adhesion

improver is blended by the alkali fusibility novolak resin (aforementioned [A]) and request 0.1 to 1.0% of the weight, especially, if 0.2 - 0.5 % of the weight is desirable and is less than 0.1 % of the weight If the adhesive improvement effectiveness over the substrate of a positive type photoresist constituent is not enough and exceeds 1.0 % of the weight, the inclination for the fall of definition and the tooth-space pattern upper part to spread is large, and since there is an inclination to generate Society for Cutting Up Men a little on the substrate after development, it is not desirable.

[0038] (D) In a sensitizer and this invention, the (D) sensitizer can be blended by request. As a sensitizer which can be used by this invention, there is especially no limit, and although it may usually be used as a sensitizer in a positive type photoresist constituent, it can be chosen as arbitration from inside. For example, the phenolic compound expressed with the following general formula (d-1) can be used.

[0039]

[Formula 4]

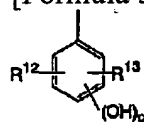


(d - 1)

[0040] Independently R1-R8 among [type, respectively A hydrogen atom, a halogen atom, the alkyl group of the carbon atomic numbers 1-6, The alkoxy group or cycloalkyl radical of the carbon atomic numbers 1-6 is expressed, and;R9-R11 express the alkyl group of a hydrogen atom or the carbon atomic numbers 1-6 independently, respectively.;Q A hydrogen atom, Residue which combines with the alkyl group of the carbon atomic numbers 1-6, and R9, and is expressed with the cyclo ring of the carbon atomic chains 3-6, or the following chemical formula (d-2)

[0041]

[Formula 5]



(d - 2)

[0042] (among a formula, R12 and R13 express the alkyl group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-6, the alkoxy group of the carbon atomic numbers 1-6, or a cycloalkyl radical independently, respectively, and;c shows the integer) of 1-3 -- expressing --; --] to which a and b express the integer of 1-3;;d expresses the integer of 0-3, and;n expresses the integer of 0-3

[0043] As a phenolic compound expressed with the above-mentioned general formula (d-1) For example, a bis(4-hydroxy - 2, 3, 5-trimethyl phenyl)-2-hydroxy phenylmethane, 1, 4-bis[1-(3, 5-dimethyl-4-hydroxyphenyl) isopropyl] benzene, 2, 4-bis(3, 5-dimethyl-4-hydroxy phenylmethyl)-6-methyl phenol, A bis(4-hydroxy - 3, 5-dimethylphenyl)-2-hydroxy phenylmethane, A bis(4-hydroxy - 2, 5-dimethylphenyl)-2-hydroxy phenylmethane, A screw (4-hydroxy - 3, 5-dimethylphenyl) -3, 4-dihydroxy phenylmethane, 1-[1-(4-hydroxyphenyl) isopropyl]-4-[1 and 1-bis(4-hydroxyphenyl) ethyl] benzene, 1-[1-(3-methyl-4-hydroxyphenyl) isopropyl]-4-[1 and 1-bis(3-methyl-4-hydroxyphenyl) ethyl] benzene, 2, 6-screw [1-(2, 4-dihydroxy phenyl) isopropyl]-4-methyl phenol, 4, 6-bis[1-(4-hydroxyphenyl) isopropyl] resorcinol, 4, 6-bis(3, 5-dimethoxy-4-hydroxy phenylmethyl) pyrogallol, 4, 6-bis(3, 5-dimethyl-4-hydroxy phenylmethyl) pyrogallol, A 2, 6-bis(3-methyl -4, 6-dihydroxy phenylmethyl)-4-methyl phenol, 2, 6-bis(2, 3, 4-trihydroxy phenylmethyl)-4-methyl phenol, 1, and 1-bis(4-hydroxyphenyl) cyclohexane etc. is mentioned. moreover -- in addition to this -- 6-hydroxy-4a-(2, 4-dihydroxy phenyl)-9-1' - SUPIRO cyclohexyl -1, 2, 3, 4 and 4a, a 9a-hexahydro xanthene, and 6-hydroxy-5-methyl-4a-(2, 4-dihydroxy-3-methylphenyl)-9-1' - SUPIRO cyclohexyl -1, 2, 3, 4 and 4a, a 9a-hexahydro xanthene, etc. can be used. These (D) sensitizers may be independent, or two or more sorts may be mixed and used, and it is desirable at the point that the combination of 1-[1-(4-hydroxyphenyl) isopropyl]-4-[1 and 1-bis(4-hydroxyphenyl) ethyl] benzene and a bis(4-hydroxy - 2, 3, 5-trimethyl phenyl)-2-hydroxy phenylmethane is excellent in the perpendicularity of high-sensitivity-izing and a tooth-space pattern especially. (D) As

for the loadings of a sensitizer, it is desirable to be preferably added in 15 - 20% of the weight of the range ten to 25% of the weight to the alkali fusibility novolak resin (above-mentioned [A]).

[0044] (E) Blend the (E) acid generator in an acid generator and this invention. As a (E) acid generator which can be used by this invention, there is especially no limit, and if heat-treatment and the exposure of a radiation decompose and an acid is generated, it can be used. In addition, when application in an actual manufacture process is considered, the compound made to generate an acid by the exposure of the same i line (365nm) as the positive type photoresist constituent of this invention is desirable. A triazine system acid generator which is indicated by JP,5-107755,A as such a (E) acid generator, for example, An oxime sulfonate system acid generator, an onium salt system acid generator, etc. are mentioned. Especially, it is 3-(methyl sulfonyl) oxy- - 1, 2, and 3-benzotriazine -4 (3H) ON It is desirable at the point that it can excel in the acid generating effectiveness also in any of heat-treatment and UV irradiation, and an acid cross-linking ingredient can be made to construct a bridge efficiently, and desirable from there being almost no effect to the property of the positive type photoresist constituent of this invention further. (E) Although the loadings of an acid generator are based also on the class, it is desirable to choose in 0.1 - 1.0% of the weight of the range preferably 0.01 to 5.0% of the weight about to a constituent (total solids).

[0045] In the positive type photoresist constituent of various addition component this inventions It aims at improvement in a remaining rate of membrane resolution and whenever [exposure allowances]. P-toluenesulfonic-acid chloride (PTSC), 4 and 4' bis[- bis(diethylamino) benzophenone, 1, and 4-] [1-(2-methyl-4-hydroxy-5-cyclohexyl phenyl) isopropyl] benzene, 1 and 3-bis[1-(2-methyl-4-hydroxy-5-cyclohexyl phenyl) isopropyl] benzene etc. may be added to a constituent by about 0.01 - 10% of the weight of within the limits, respectively.

[0046] moreover, in the positive type photoresist constituent of this invention The ultraviolet ray absorbent for the additive which is furthermore compatible if needed, for example, antihalation, For example, 4-dimethylamino - 2', a 4'-dihydroxy benzophenone, A 5-amino-3-methyl-1-phenyl-4-(4-hydroxy phenylazo) pyrazole, A 4-dimethylamino-4'-hydroxyazobenzene and 4-diethylamino -4'-ethoxy azobenzene, Moreover, the surfactant for striae SHON prevention, [curcumine / a 4 and 4'-diethylamino azobenzene,] For example, Fluorad FC-430, FC431 (a trade name, product made from Sumitomo 3M), EFUTOPPU EF122 -- A and EF122 -- B and EF122 -- addition content of the fluorochemical surfactants, such as C, EF126 (a trade name, product made from TOKEMU Products), and the megger fuck R-08 (Dainippon Ink & Chemicals, Inc. make), etc. can be carried out in the range which does not have trouble in the purpose of this invention.

[0047] As for the positive type photoresist constituent of this invention, it is desirable to dissolve in a suitable solvent and to use a (A) component - (E) component and the various addition components added if needed in the form of a solution. As an example of such a solvent, the solvent used for the conventional positive type photoresist constituent can be mentioned. For example, an acetone, a methyl ethyl ketone, a cyclohexanone, methyl isoamyl ketone, Ketones, such as 2-heptanone; Ethylene glycol, propylene glycol, Diethylene-glycol and ethylene glycol mono-acetate, propylene glycol mono-acetate, Diethylene-glycol mono-acetate or these monomethyl ether, Polyhydric alcohol and the derivatives of those, such as the monoethyl ether, the monopropyl ether, the monobutyl ether, or the monophenyl ether; Ring type ether; and ethyl lactate like dioxane, Ester, such as methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, pyruvic-acid ethyl, methoxy methyl propionate, and ethoxy ethyl propionate, can be mentioned. These may be used independently, and may mix and use two or more sorts. Ester, such as ketones; ethyl lactates, such as an acetone, a methyl ethyl ketone, a cyclohexanone, methyl isoamyl ketone, and 2-heptanone, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, pyruvic-acid ethyl, methoxy methyl propionate, and ethoxy ethyl propionate, is especially desirable. In addition, although a solvent may be used independently, in order to obtain 3.0 micrometers or more and membrane formation nature especially good on about 6.0-8.0-micrometer thick-film conditions, you may use combining two or more sorts of solvents.

[0048] If an example is shown about the suitable operation of the positive type photoresist constituent of this invention On substrates, such as Si, copper, and an iron nickel alloy, first, the alkali fusibility novolak resin (above-mentioned [A]), The solution melted into the above-mentioned (E) acid generator and a suitable solvent which described above the various addition components added if needed is applied with a spinner etc. Dry, a sensitization layer is made to form and, subsequently the light of the wavelength near 365nm is exposed through a desired mask pattern using the light source which emits light, for example, a low pressure mercury lamp, a high pressure mercury vapor lamp, and an ultrahigh pressure mercury lamp. Next, an image faithful to a mask pattern can be obtained by performing PEB (exposure afterbaking) processing, immersing this in a developer, for example, an alkaline water solution like a 1 - 10-

% of the weight tetramethylammonium hydroxide (TMAH) water solution, and carrying out dissolution removal of the exposure section.

[0049] Next, by request, although the coat of an acid cross-linking ingredient is formed all over the formed tooth-space pattern, before forming said coat, complete exposure or alternative exposure may be performed to said tooth-space pattern. Or after forming said coat, complete exposure or alternative exposure may be performed. According to the class of acid generator to be used, a suitable thing should just be used for the wavelength used for exposure that the acid generator in a tooth-space pattern should just be the wavelength which generates an acid. After forming the coat of an acid cross-linking ingredient, it heat-treats and the part which touches the tooth-space pattern of said acid cross-linking ingredient according to an operation of the acid diffused from a tooth-space pattern front face is made to construct a bridge. Here, as an acid cross-linking ingredient used, if it comes to contain the water-soluble resin which causes crosslinking reaction with an acid, and the water-soluble cross linking agent which produces bridge formation with an acid, it is desirable. As for the water-soluble suitable resin used here, polyacrylic acid, a polyvinyl acetal, a polyvinyl pyrrolidone, polyvinyl alcohol, polyethyleneimine, a styrene maleic anhydride copolymer, a polyvinyl amine, the poly allylamine, oxazoline radical content water soluble resin, water-soluble urethane, a water-soluble phenol, water-soluble epoxy, water-soluble melamine resin, a water-soluble urea-resin, an alkyd resin, a sulfonamide and one sort of these Shio, or two sorts or more of mixture is mentioned. Moreover, said water-soluble cross linking agent can be used as one kind or two kinds or more of such mixture, although there is especially no limitation, for example, amino system cross linking agents, such as urea system cross linking agents, such as melamine system cross linking agents, such as a melamine derivative and a methylol melamine derivative, a urea derivative, a methylolurea derivative, an ethylene urea carboxylic acid, and a methylol ethylene urea derivative, isocyanate, benzoguanamine, and glycoluryl, etc. are mentioned. Furthermore, it is desirable to add a surfactant into an acid cross-linking ingredient in respect of striae SHON prevention. For example, the megger fuck R-08 is mentioned. Next, the tooth-space pattern of width of face narrower than the tooth-space width of face of the tooth-space pattern before forming the coat of an acid cross-linking ingredient can be formed by dissolving said acid cross-linking ingredient of the field which is not constructing a bridge using the developer from which said acid cross-linking ingredient of the field which is not constructing a bridge is removable. In addition, as said developer, there is especially no limitation, is the range in which the tooth-space pattern of a substrate is not dissolved, and should just use the solution which mixed water, water, and alcohols, or a mixed solution with independent or water of a water-soluble organic solvent. For example, it is appropriate for said alcohols to use a methanol, ethanol, propanol, a butanol, etc., and N-methyl pyrrolidone, 2-heptanone, an acetone, etc. are mentioned to said water-soluble organic solvent.

[0050]

[Example] Hereafter, an example and the example of a comparison explain this invention further. In addition, many physical properties of a positive type photoresist constituent were searched for as follows.

(1) Cross-section configuration evaluation : the sample was applied on the iron nickel alloy substrate using the spinner, this was dried for 90 seconds 100 degrees C on the hot plate, and the resist film of 6.0 micrometers of thickness was obtained. Subsequently, after exposing on this film using contraction projection aligner NSR-2005i10D (the NIKON CORP. make, NA=0.50) through a mask (for the tooth-space pattern formation of 0.35-micrometer width of face) with a mask dimension of 0.35 micrometers, having applied bias so that a pattern pars basilaris ossis occipitalis may be finished to the tooth-space pattern of 0.50-micrometer width of face, 100 degrees C and 90-second Hazama's PEB (exposure afterbaking) processing were performed. Subsequently, after applying the tetramethylammonium hydroxide (TMAH) water solution on the substrate 2.38 23-degree C% of the weight and holding for 60 seconds as development actuation, rotation of a spinner performed the swing end. After repeating this development actuation 5 times, it rinsed for 30 seconds, and it dried and the tooth-space pattern whose dimension of a pattern pars basilaris ossis occipitalis is 0.50-micrometer width of face was formed. Subsequently, spinner spreading of the solution of an acid cross-linking ingredient was carried out all over said tooth-space pattern top, desiccation processing was performed for 70 seconds at 85 degrees C, and the paint film of 0.25 micrometers of thickness was formed. Next, after it heat-treated 90-second Hazama at 120 degrees C and pure water washed after that, the cross-section configuration of the tooth-space pattern obtained by heat-treating 90-second Hazama at 90 degrees C was observed with the SEM (scanning electron microscope) photograph, and the dimension of a tooth-space pattern pars basilaris ossis occipitalis was measured. Moreover, the ratio (B/M) of the width of face (B) of the pattern pars basilaris ossis occipitalis to the width of face (M) of pattern CHUBU ENGINEERING CORPORATION (place whose height is 3.5 micrometers from a pattern pars

basilaris ossis occipitalis to the direction of thickness) That by which a pattern pars basilaris ossis occipitalis was not able to form [the thing of $0.70 \leq (B/M) \leq 1.0$] O and the thing of $(B/M) < 0.65$ in the tooth-space pattern of ** and 0.50-micrometer width of face for O and the thing of $0.65 \leq (B/M) < 0.70$ was expressed as xx. In addition, the mimetic diagram showing the cross-section configuration of a tooth-space pattern was shown in drawing 1 . In addition, as for a substrate and 2, in drawing 1 , 1 is [a resist paint film and 3] a tooth-space pattern and 4 acid cross-linking ingredient film.

[0051] (Synthetic example 1) composition (m-cresol /p-cresol/-- 2, 3, and 5-trimethyl phenol =35/-- 40/25 (mole ratio)) of alkali fusibility novolak resin $M_w=4200$, $M_w/M_n=2.3$, 1 to the hydrogen atom of all phenolic hydroxyl groups, the weight average molecular weight by substitutional rate =3.8 mol %1. judgment actuation of 2-naphthoquinonediazide sulfonyl group (M_w), The control m-cresol of degree of dispersion (M_w/M_n), p-cresol, Polycondensation (product a) ($M_w=2600$, $M_w/M_n=3.3$) 125g compounded by the dehydration condensation reaction of a 2, 3, and 5-trimethyl phenol (mole ratio 35:40:25) and formalin is put into a 2l. beaker. Methanol 920g was blended with this and it was made to dissolve using an agitator. Subsequently, added 313g of pure water, precipitate was made to generate, this was taken out, and the polycondensation product (b) by which molecular weight and degree of dispersion were controlled, and ($M_w=4200$, $M_w/M_n=2.3$) were obtained. In addition, the phenol system monomer called for from GPC measurement and the content of a dimer were 0.49 % of the weight and 2.72 % of the weight, respectively.

[0052] In addition, following equipment and conditions performed GPC measurement.

[M_w , the measurement means of GPC in M_w/M_n measurement]

(1) Dissolve 20mg of samples in THF10ml, and adjust the sample solution.

20micro of sample solutions 1 of (2) and (1) was poured into the following GPC measuring device, and the elution time amount of the sample which passes for 35 minutes and is detected near UV wavelength of $\lambda = 280\text{nm}$ was measured.

(Measuring device) a guard column (product made from product name "KF-G";Shodex), and three separation columns (column size 8micrometer(path) x which used the styrene-divinylbenzene copolymer of 6-micrometer particle size as the bulking agent -- 300mm (die length)) It has a product made from product "KF-805 name s";Shodex. Separation column temperature The liquid-sending rate of the eluate of a tetrahydrofuran (THF) was performed on condition that 1.0 ml/min using the GPC measuring device (product made from product name "GPC SYSTEM 11";Shodex) set as 35 degrees C using oven.

[0053] [A phenol system monomer, the measurement means of GPC in the amount measurement of dimers]

(1) Dissolve 20mg of samples in THF10ml, and adjust the sample solution.

10micro of sample solutions 1 of (2) and (1) was poured into the following GPC measuring device, and the elution time amount of the sample which passes for 28 minutes and is detected near UV wavelength of $\lambda = 280\text{nm}$ was measured.

(Measuring device) a guard column (product made from product name "KF-G";Shodex), and three separation columns (column size 8micrometer(path) x which used the styrene-divinylbenzene copolymer of 6-micrometer particle size as the bulking agent -- 300mm (die length)) It has a product made from product name "KF-801";Shodex. Separation column temperature The liquid-sending rate of the eluate of a tetrahydrofuran (THF) was performed on condition that 1.0 ml/min using the GPC measuring device (product made from product name "GPC SYSTEM 11";Shodex) set as 40 degrees C using oven.

[0054] 2. Substitution reaction aforementioned polycondensation product (b) It put into the 1l. three-neck flask with which the thermometer, the agitator, and the dropping funnel attachedg [50], 1, and 2-naphthoquinonediazide-5-sulfonic-acid chloride 4g (0.015 mols), and after adding dioxane 162g to this and making it dissolve in it, triethylamine 3.0g (0.030 mols) was added from the dropping funnel, and stirring was continued at the room temperature for 2 hours. Then, after adding 4.7g (0.045 mols) of 35% hydrochloric-acid water solutions of concentration and continuing stirring at a room temperature further for 30 minutes, the dark reddish-brown liquid was obtained by carrying out a ** exception. In addition, precipitate was deposited, stirring said liquid to the 2l. beaker containing 1l. of pure water. After carrying out said sediment the ** exception and dissolving the obtained solid content in butyl acetate, the solution was condensed, ethyl lactate was added further and the solution of the alkali fusibility novolak resin with which 3.8-mol% of the hydrogen atom of all hydroxyl groups was permuted by 1 and 2-naphthoquinonediazide sulfonyl group which used the mixed solution (mixing ratio 2:8) of butyl-acetate-ethyl lactate as the solvent was obtained.

[0055] (Synthetic example 2) The synthetic tetrapod (hydroxymethyl) glycoluryl (product [made from Mitsui

SAITEKKU], trade name "Cymel 1172") 20 weight section of an acid cross-linking ingredient, the polyvinyl-acetal resin (Sekisui Chemical Co., Ltd. make, trade name "S lek KW-1") 80 weight section, and a nonionic fluorine and the silicone system surfactant (Dainippon Ink & Chemicals, Inc. make, trade name "the megger fuck R-08") 0.1 weight section were dissolved in the water 1900 weight section, and it considered as the water solution of 5 % of the weight of solid content. Subsequently, when an aperture filtered using the membrane filter which is 0.2 micrometers, the acid cross-linking ingredient was obtained.

[0056]

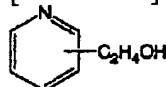
(Example 1)

(A) Component: The 100 weight sections (the 200g of the 50 % of the weight alkali fusibility novolak resin solutions of concentration of the synthetic example 1)

(B) Component: The 8.05 weight sections (benzyl salicylate)

(C) Component: 0.25 weight section [2-(2-hydroxyethyl) pyridine] [0057]

[Formula 6]



[0058]

(D) Component : 15 weight sections 1-[1- Mixture (E) component of isopropyl]-4-[1 and 1-bis(4-hydroxyphenyl) ethyl] benzene / bis(4-hydroxy - 2, 3, 5-trimethyl phenyl)-2-hydroxy phenylmethane =1 / 1 (weight ratio) : (4-hydroxyphenyl) The 0.50 weight sections (3-(methyl sulfonyl) oxy-- 1, 2, 3-benzotriazine -4 (3H) ON)

After dissolving each above-mentioned component in the ethyl lactate-butyl-acetate mixed solvent (mixing ratio 2:8) 55 weight section, this was filtered using the membrane filter of 0.1-0.2 micrometers of apertures, and the positive type photoresist constituent was prepared.

[0059] (Examples 2 and 3) Instead of the (E) acid generator used in the example 1, the positive type photoresist constituent was prepared like the example 1 except having used alpha [(methyl sulfonyl) oxy-] imide] benzene acetonitrile (example 2) and the JI (n-butyl sulfonyl) dimethylglyoxime (example 3), respectively.

[0060] (Example 4) The positive type photoresist constituent was prepared like the example 1 except having replaced the addition of the (E) acid generator with the 0.2 weight section.

[0061] (Example 5) The positive type photoresist constituent was prepared like the example 1 except having replaced the addition of the (E) acid generator with the 0.7 weight section.

[0062] (Example 1 of a comparison) The positive type photoresist constituent was prepared like the example 1 except having not added the (E) acid generator.

[0063] (Example 2 of a comparison) The positive type photoresist constituent was prepared like the example 1 except having used one mol of 2, 3, and 4-trihydroxy benzophenones, and the 2.0 mols [of 1 and 2-naphthoquinonediazide-5-sulfonic-acid chloride] esterification object 10 weight section as the polycondensation (product b) 100 weight section compounded in the synthetic example 1 instead of and a photosensitive component. [the (A) component used in the example 1]

[0064] Evaluation of positive type photoresist constituent ***** prepared above in examples 1-5 and the examples 1 and 2 of a comparison and the above (1) was performed, and the result was shown in Table 1.

[0065]

[Table 1]

	(1) 断面形状 膜厚6.0μm (パターン底部の寸法(幅))
実施例 1	◎ (0.30μm)
// 2	○ (0.35μm)
// 3	◎ (0.30μm)
// 4	◎ (0.35μm)
// 5	○ (0.30μm)
比較例 1	◎ (0.45μm)
// 2	×× (— μm)

[0066] When the constituent of examples 1-5 was used a passage clear from the result of Table 1, the cross-section configuration was good and it turned out that it is what is excellent in thermal resistance. Moreover, in the process using an acid cross-linking ingredient, bridge formation advanced efficiently, ** tooth-space patternizing was realized, and the tooth-space pattern of a very high aspect ratio was formed.

[0067]

[Effect of the Invention] According to this invention, the 3.0 micrometers or more of the formation approaches of the positive type photoresist constituent [under about 6.0-8.0-micrometer thick-film conditions, excel in thermal resistance, and formation of a tooth-space pattern with the sufficient generating effectiveness of an acid is possible, and] which can form the tooth-space pattern which is a high aspect ratio with a width of face of 0.8 micrometers or less with sufficient perpendicularity, a substrate with the photosensitive film, and a resist pattern are offered especially.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the mimetic diagram showing the scale of cross-section configuration evaluation of a tooth-space pattern.

[Description of Notations]

- 1 Substrate
 - 2 Resist Paint Film
 - 3 Tooth-Space Pattern
 - 4 Acid Cross-linking Ingredient Film
-

[Translation done.]

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WRITTEN AMENDMENT

----- [a procedure revision]
[Filing Date] July 27, Heisei 13 (2001. 7.27)
[Procedure amendment 1]
[Document to be Amended] Specification
[Item(s) to be Amended] 0057
[Method of Amendment] Deletion

[Translation done.]